A New Compound of Uranium VI with Formamide UO$_3$ · HCONH$_2$ · 0.5H$_2$O

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A new compound of uranium VI has been prepared by thermolysis of uranyl formate diammoniate in an ammonia environment. Chemical analysis and infrared spectrophotometry favor the formula UO$_3$ · HCONH · 0.5H$_2$O. X-Ray analysis is in agreement with an orthorhombic lattice having parameters $a = 6.88$ Å, $b = 23.46$ Å, $c = 24.67$ Å. The photoluminescence spectra of this compound are presented.

1. Introduction

Using the framework of a thorough study undertaken in this Laboratory on the solid state photochemistry of uranyl formate monohydrate (*1, 2*) we were led to assume that the water molecule coordinated to the uranyl group (*3*) could favor electron transfer provoking the reduction of uranium, and that, on the contrary, carbon dioxide could inhibit this transfer (*4*). It is therefore very tempting to generalize this working hypothesis in assuming that Lewis bases accelerate the photoreduction, whereas Lewis acids slow down this process. This is why we began by studying the influence of NH$_3$ on the photoreduction of anhydrous uranyl formate. Effectively, we confirmed its accelerating role at room temperature.

However, the ammonia action goes further, since it transforms the anhydrous uranyl formate into the diammoniate UO$_2$(HCOO)$_2$ · 2NH$_3$, already described (*5*) and labeled as UFDA in the following, which evolves ammonia at higher temperature, yielding a novel compound which is reported here.

2. Experimental

Uranyl formate monohydrate is prepared according to the method recommended by Sahoo *et al.* (*6*). About 1 g of this salt is put into a boat and introduced into a tube located in a temperature-regulated furnace and linked on one side to a conventional vacuum device and, on the other side, to a gas line which allows the admission of ammonia (99.9% by volume). Uranyl formate monohydrate is first dehydrated by heating at 150°C in a vacuum of 10^{-2} Torr for 2 hr. The anhydrous salt is then maintained at room temperature under 1 atm of NH$_3$ for 1 h. A yellow-orange solid is thus obtained, whose X-ray diffraction pattern and differential thermal analysis (DTA) are in agreement with those already described for UO$_2$(HCOO)$_2$ · 2NH$_3$ (*5*). Under mechanical pump vacuum, this compound is not stable and can lose at least 1 mole of ammonia in 48 hr. Exposed to polychromatic irradiation of a mercury lamp (Philips HPK 125) it decomposes, leading to U^V and U^{IV} in amounts noticeably larger than uranyl formate monohydrate (*4*). This could be

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related to the more basic character of ammonia compared to water.

When uranyl formate diammoniate is heated under 1 atm of NH_3 the solid is observed to turn orange at 100°C, and there is evolution of a gas condensable at room temperature. In order to get the order of magnitude of the temperature which is needed to complete formation of this new solid, S, we carried out a DTA on anhydrous uranyl formate under an ammonia atmosphere, in a BDL M.3 device. As shown by Fig. 1 a strong endotherm, which ends at 180°C, is observed. Thus, the preparation of S was resumed with UFDA as the starting material in the previously described setup at a constant temperature of 170°C. Infrared absorption spectrophotometry and mass spectrometry of the liquid condensed from the evolved gas phase show that it consists of formamide and water. The weight loss between UFDA and S is 13.2% of the initial weight.

The chemical analysis of S is effected for uranium by calcination into U_3O_8 (7) and for carbon, hydrogen, and nitrogen by conventional organic microanalysis. The results are as follows:

	Composition (wt%)			
	U	C	H	N
Experimental for S	69.5	3.64	1.16	3.97
Calculated for $U_2O_9C_2H_8N_2$	70.00	3.53	1.18	4.12

3. Infrared and X-ray Analysis of S

3.1. Infrared absorption spectra are obtained for S dispersed in a KBr matrix with a Perkin–Elmer 257 spectrophotometer and the recorded bands are shown in Table I. We observe:

—the absence of the asymmetric vibration ν_{as} of the UO_2^{2+} ion, usually located at 950–930 cm^{-1}, which establishes that S is not an uranyl salt, although it is indeed an oxygenated compound of uranium, as shown by the broad band at 848 cm^{-1} characteristic of the U–O stretching vibration;

—the presence of an important peak between 3000 and 3500 cm^{-1} which characterizes the vibrations $\nu(OH)$ of water and $\nu(NH)$ of formamide;

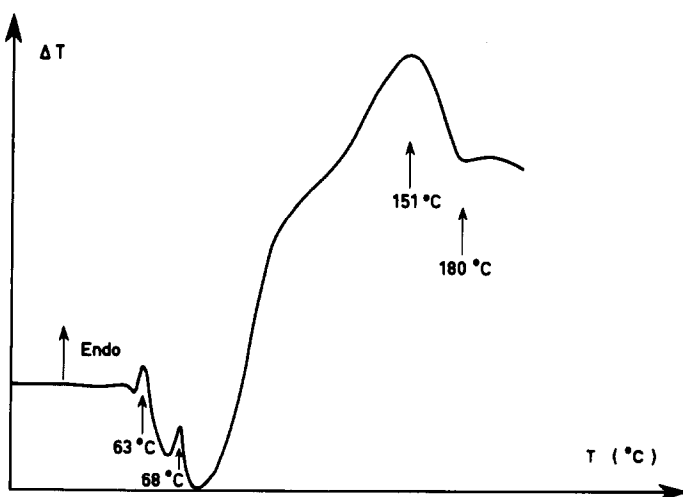FIG. 1. DTA of $UO_2(HCOO)_2 \cdot 2NH_3$ in dry ammonia. Reference, Al_2O_3. Heating rate, 10°C min^{-1}.

TABLE I

COMPARED INFRARED SPECTRA OF FORMAMIDE $HCONH_2$ AND $UO_3 \cdot HCONH_2 \cdot 0.5H_2O$ $(T = 298$ K$)$

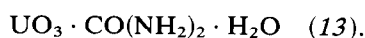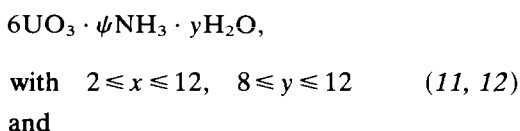| Formamide (liquid)			$UO_3 \cdot HCONH_2 \cdot 0.5H_2O$			
I^a	cm^{-1}	Ascription	I^a	cm^{-1}	Ascription	References
s	3425⎫	$\nu_{as}(NH)$	m	3340	$\nu_{as}(NH)$	
s_{sd}	3340⎭		m	3290⎫	$\nu(OH)$	
			s	3220⎭		
m_{sd}	3190	$\nu_s(NH)$	s	3170	$\nu_s(NH)$	
			m_{sd}	3025		
w_{sh}	2900⎫	$\nu(CH)$	w_{sd}	2770	$\nu(CH)$	
vw	2780⎭		w_{sd}	2680		
vs_{sd}	1700⎫	$\nu(CO) + \nu(CN)$	s	1695	$\nu(CO)$	
vs	1690⎭					
m_{sd}	1620	$\delta(NH_2)$	m	1604	$\delta(HOH)$	
			vs	1540	$\nu(NH_2) + \nu(CN)$	(8, 9)
			m_{sd}	1403⎫	$\nu(CO) + \nu(CN)$	(8, 9)
			s_{sh}	1380⎭		
m_{sh}	1397					
m	1315		m	1350		
			w	1100	$\pi(CH)$	
vw	1090	$\pi(CH)$	w	1050	$\rho_w(NH_2)$	(8)
w_{sh}	1050		vs	848⎫		
			m_{sd}	800�	$\nu(UO)$	
			m	782⎬		
			m	758⎭		
			w	687	$\rho(H_2O) + \rho_r(NH_2)$	(8)

[a] v, very; s, strong; m, medium; w, weak; sd, shoulder; sh, sharp.

—the presence of several bands which may be ascribed to coordinated formamide. These findings lead us for the new compound S to the formula $UO_3 \cdot HCOHN_2 \cdot 0.5H_2O$ rather than $U_2O_7(HCONH_3)_2$ the $HCONH_3^+$ cation being relatively unstable (10). Its formation would then occur according to the stoichiometric equation

$$UO_2(HCOO)_2 \cdot 2NH_3 \xrightarrow{\ NH_3(g)\ }$$
$$UO_3 \cdot HCONH_2 \cdot 0.5H_2O$$
$$+ HCONH_2 + 0.5H_2O, \quad (1)$$
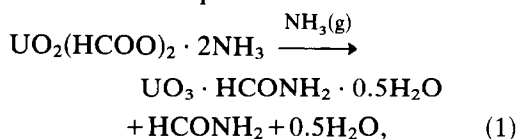
with a theoretical weight loss of 13.7% which is in good agreement with the previously reported experimental weight loss (13.2%). From the mechanistic point of view, the transformation of the formate anion and ammonia ligand into formamide in the solid state is remarkable. It is likely that ammonia from the gas phase plays a role in this transformation, since the presence of an ammonia atmosphere is necessary for reaction (1) to take place. In the absence of ammonia, thermolysis of UFDA leads to a different product which could be $UO_2(OH)$ $(HCOO)NH_3$, according to Wiel (5), whose analytical results are not, however, completely convincing. It is also worth noticing that compounds analogous to S have already been obtained, e.g.,

$$6UO_3 \cdot \psi NH_3 \cdot yH_2O,$$

with $2 \leq x \leq 12$, $8 \leq y \leq 12$ (11, 12) and

$$UO_3 \cdot CO(NH_2)_2 \cdot H_2O \quad (13).$$

3.2. An X-ray Debye–Scherrer pattern has been obtained and Table II gathers the first 25 observed lines. These lines could be indexed with the help of the POWDER computer program (14). The lattice found is orthorhombic with the following

parameters:

$$a = 6.88 \text{ Å}, \quad b = 23.45 \text{ Å}, \quad c = 24.67 \text{ Å}.$$

The measured density is 3.973 g cm^{-3}, which leads to 14 units $2UO_3 \cdot 2HCOHN_2 \cdot H_2O$ per cell P. The quadratic form is:

$$10^5 \sin^2 \theta = 1255.58h^2 + 108.02k^2 + 97.62l^2.$$

No extinction rule has been observed.

In the analogous case of $UO_3 \cdot aNH_3 \cdot yH_2O$, Debets and Loopstra (15) found that the lattices of these compounds could be explained as deriving from that of $\alpha\text{-}UO_3$, which is orthorhombic (16) with the parameters:

$$a' = 3.913 \text{ Å}, \quad b' = 6.936 \text{ Å}, \quad c' = 4.167 \text{ Å}.$$

In our case, it would also be possible to derive the lattice of S from that of $\alpha\text{-}UO_3$ by the operations:

$$a \simeq b', \quad b \simeq 6a', \quad c \simeq 6c'.$$

These relations support the proposed formula: formamide and water would enter the $\alpha\text{-}UO_3$ cell in expanding without appreciably distorting it; this is a well-known characteristic of intercalation compounds.

4. Some Properties of S

4.1. S is not soluble in formamide or dimethylformamide, but it dissolves readily in anhydrous formic acid to give anhydrous uranyl formate. It is slowly hydrolyzed in water to give an ammonium uranate, the composition of which is close to the already mentioned

$$6UO_3 \cdot 2NH_3 \cdot 10H_2O \quad (12).$$
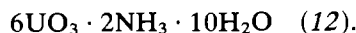
4.2. In dry air at room temperature S is very stable, and does not undergo any observable photodecomposition. When submitted to 366-nm wavelength irradiation it exhibits at 300°K an intense green luminescence, constituting a single broad
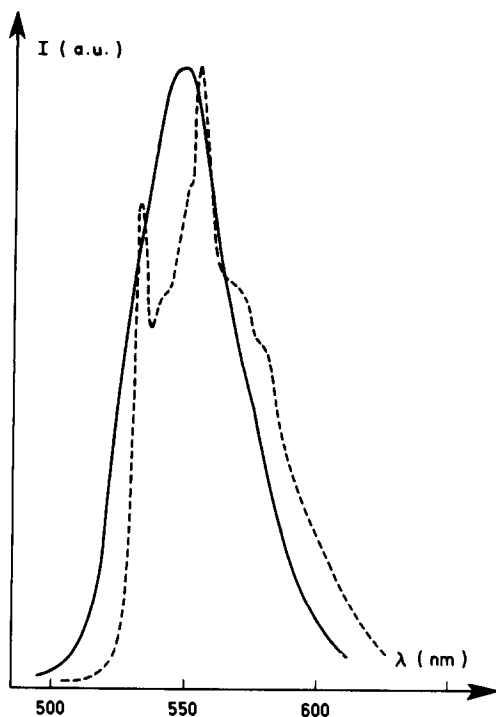
TABLE II

X-RAY DIFFRACTION DIAGRAM OF $UO_3 \cdot HCONH_2 \cdot 0.5H_2O^a$

	$10^5 \sin^2 \theta$		d (Å)			
I^b	Obs	Calc	obs	h	k	l
w	526	530	10.63	0	2	1
m	1060	1070	7.49	0	3	1
Vs	1307	1311	6.74	0	2	3
w	1370	{1364 / 1363}	6.59	{1 / 0}	{1 / 3}	{0 / 2}
vw	1780	1785	5.78	1	2	1
w	2567	2566	4.811	1	2	3
w	3365	3374	4.203	1	4	2
vw	3818	3804	3.945	1	1	5
vw	4040	4054	3.835	1	5	1
vw	4117	4128	3.799	1	2	5
s	4698	4668	3.557	1	3	5
vw	4856	4835	3.498	1	5	3
m	5041	5022	3.433	2	0	0
vw	5189	5202	3.384	1	2	6
s	5714	5742	3.225	1	3	6
m	5976	5995	3.153	2	3	0
s	6358	6356	3.057	0	1	8
vw	7586	{7571 / 7585 / 7611}	2.799	{2 / 1 / 1}	{1 / 6 / 1}	{5 / 5 / 8}
m	9750	9731	2.469	1	8	4
s	10694	10706	2.357	2	7	2
vw	12645	{12611 / 12663}	2.168	{3 / 3}	{2 / 3}	{3 / 2}
vw	13080	{13052 / 13070 / 13068}	2.132	{1 / 0 / 1}	{6 / 11 / 0}	{9 / 0 / 11}
vw	13435	{13419 / 13461}	2.103	{3 / 0}	{4 / 11}	{2 / 2}
vw	14509	{14498 / 14513}	2.024	{1 / 0}	{10 / 5}	{5 / 11}
w	15120	15099	1.983	2	7	7

^{a} Cu$K\bar{\alpha}$ radiation, $\lambda = 1.5418$ Å; Debye–Scherrer camera of 360-mm circumference; intensities visually estimated and corrected for absorption.

^{b} V,v very; s, strong; w, weak; m, medium.

FIG. 2. Corrected photoluminescence spectra of $UO_3 \cdot HCONH_2 \cdot 0.5H_2O$ under a 366-nm wavelength irradiation. Solid line, room temperature; broken line, liquid nitrogen temperature.

band peaking at 550 nm which is resolved at 77°K into several bands (Fig. 2). The vibronic spectrum characteristic of uranyl salts (17) is absent, which confirms the absence of UO_2^{2+} ions. Photoluminescence of S is very different from that of the hydrated oxides $UO_3 \cdot nH_2O$ (18) and seems more related to the luminescence of U^{6+} in an octahedral environment (19).

4.3. When submitted to DTA in dry air (Fig. 3) S undergoes a strongly exothermic reaction at about 330°C, which coresponds, as gravimetrically and X-ray analytically determined, to $UO_{2.9}$ (20). The endotherm observed at 620°C corresponds to the formation of U_3O_8, as confirmed by X rays and TGA.

5. Conclusion

A new compound of uranium has been prepared, the analysis of which, by chemical titration and IR spectrophotometry, is in agreement with the formula $UO_3 \cdot HCONH_2 \cdot 0.5$. The existence of numerous ammonium uranates
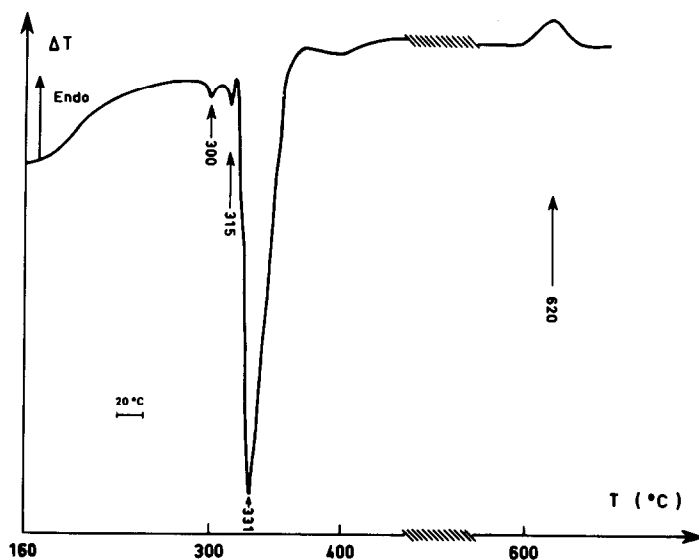

FIG. 3. DTA of $UO_3 \cdot HCONH_2 \cdot 0.5H_2O$ in dry air. Reference, Al_2O_3. Heating rate, 10°C min^{-1}.

of different compositions leads us to assume that a series of such compounds may be found in the ternary diagram UO_3–$HCONH_2$–H_2O.

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